

Actinoids

Actinides / Actinoids / Actinones / Transuranium elements / Superheavy elements (SHE)

15 elements \rightarrow $_{89}\text{Ac}$, $_{90}\text{Th}$, $_{91}\text{Pa}$, $_{92}\text{U}$, $_{93}\text{Np}$, $_{94}\text{Pu}$, $_{95}\text{Am}$,
 $_{96}\text{Cm}$, $_{97}\text{Bk}$, $_{98}\text{Cf}$, $_{99}\text{Es}$, $_{100}\text{Fm}$, $_{101}\text{Md}$, $_{102}\text{No}$, $_{103}\text{Lr}$

Outer electronic configuration: $[\text{Rn}] 5f^{0-14} 6d^{0-2} 7s^2$
 The fifteen elements from Ac ($Z=89$) to Lr ($Z=103$) in which the $5f$ orbitals are being filled up are called actinide series. The name actinide is derived from actinium, the very first member of the series. Only the first four elements, namely actinium, thorium, protoactinium and uranium are found in nature in considerable amount. Others are trace elements or made artificially by nuclear bombardment. All the actinides are radioactive and toxic to humans.

Electronic Configuration

After Hg, we follow 6 elements from Tl to Rn in which e^- enter the $6p$ subshell. Rn has the configuration $[\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^6$. At this stage, the $7s$ and $6d$ subshells have smaller energy relative to the $5f$ subshell and the next two e^- are added to the $7s$ subshell, as we get Fr and Ra which are s-block elements indeed. We find that, $5f$ and $6d$ subshells penetrate the $7s$ orbital quite significantly and are therefore stabilised compared to the $7p$ subshell. The next few electrons, thus, enter either of these two subshells i.e. $5f$ and $6d$. It soon becomes obvious that, as we fill electrons from Ac onwards, the energies of $6d$ and $5f$ do not vary significantly and allocation of electrons to determine actual electronic configuration becomes difficult. Thus, there is indeed confusion and different authors suggested different configurations.

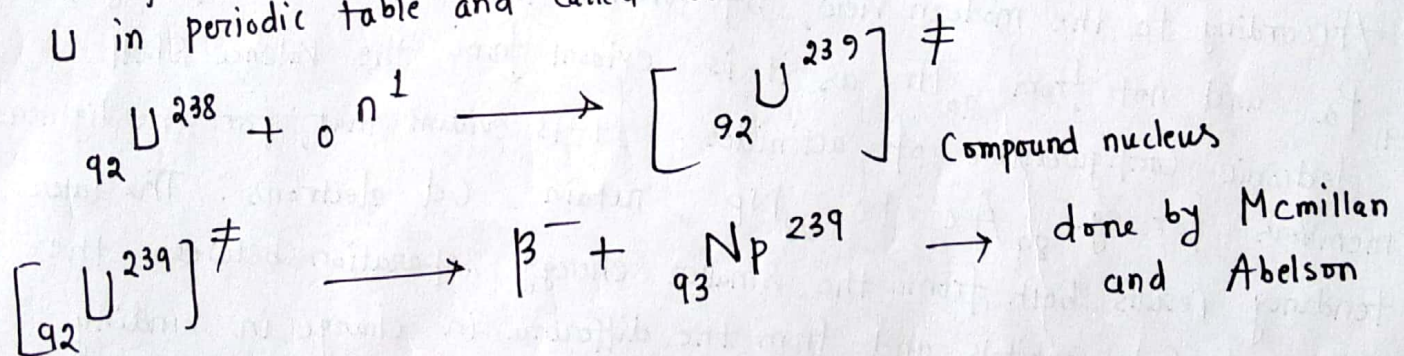
element	atomic no.	electronic configuration
1) Ac	89	$[Rn] 5f^0 6d^1 7s^2$
2) Th	90	$[Rn] 5f^0 6d^2 7s^2$
3) Pa	91	$[Rn] 5f^2 6d^1 7s^2$
4) U	92	$[Rn] 5f^3 6d^1 7s^2$
5) Np	93	$[Rn] 5f^4 6d^1 7s^2$
6) Pu	94	$[Rn] 5f^6 7s^2$
7) Am	95	$[Rn] 5f^7 7s^2$
8) Cm	96	$[Rn] 5f^7 6d^1 7s^2$
9) Bk	97	$[Rn] 5f^9 7s^2$
10) Cf	98	$[Rn] 5f^{10} 7s^2$
11) Es	99	$[Rn] 5f^{11} 7s^2$
12) Fm	100	$[Rn] 5f^{12} 7s^2$
13) Md	101	$[Rn] 5f^{13} 7s^2$
14) No	102	$[Rn] 5f^{14} 7s^2$
15) Lr	103	$[Rn] 5f^{14} 6d^1 7s^2$

(3)

An important point is that, around Ac, both 6d and 5f subshell are of very similar energies, but as we keep filling the elements, the 5f subshell definitely acquires greater stability as atomic number increases. From Uranium onwards, there is no doubt that the 5f subshell is more stable. In case of actinium, Th, Am, Bk, Cf and Es, the configurations were determined from an analysis of spectroscopic data obtained from the emission lines from neutral and charged gaseous atoms. The knowledge of the electronic structures from Pa, Np, Pu, Cm, Fm results from atomic beam experiments.

Identification and nuclear synthesis of the elements

Among the naturally occurring elements, U has the highest atomic no. = 92. For this reason, the element continued to occupy last position in the periodic table for a pretty long time. Since 1940, 11 elements with atomic no. = 93, 94, 95, 96, 97, 98, 99, 100, 101, 102 and 103 have been identified and synthesised by the transformation of the naturally occurring elements and placed beyond U in periodic table and called as transuranium elements.



Physical and chemical properties

① Oxidation States

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						(2)			(2)	(2)	(2)	(2)	(2)	
<u>3</u>	3	(3)	(3)	3	3	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	3	3	3	3	3
	4	4	4	4	<u>4</u>	4	4	4	(4)					
		<u>5</u>	5	<u>5</u>	5	5								
		<u>6</u>	<u>6</u>	<u>6</u>	6	6								

Parenthesis \rightarrow solid state only but not well characterised
underlined \rightarrow most common oxidation state

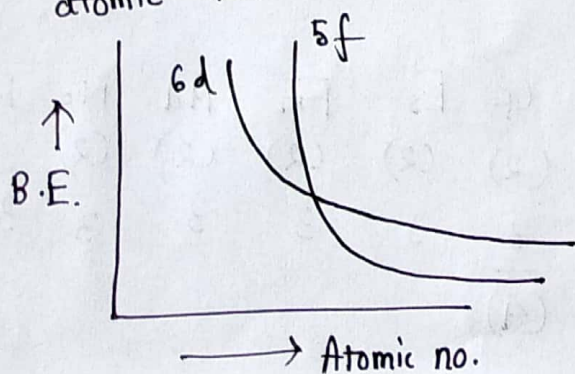
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Np, Pu and Am can show +7 oxdn. state also rarely.

The span of oxidation states of the actinoids is somewhat complicated. The +4 state of Cm is limited to CmO_2 and CmF_4 in solid state and an ion is stable only in highly complexing aqueous soln. The +4 state of Cf is limited only to CfO_2 , CfF_4 and in some double salts such as $7\text{NaF} \cdot 6\text{CfF}_4$. In the 2nd half of the actinide series the +2 state first appears in the form of solid compounds and Cf becomes successively most stable in proceeding to No. The +II state is observed in aq. soln. for Fm, Md and No. The existence of Am(II) and Bk(IV) demonstrate the stability of the half-filled $5f^7$ configuration i.e. $5f^7$. The fact, that the +II state is the most stable oxdn. state for No, shows the stability associated with the filled $5f$ configuration i.e. $5f^{14}$.

Nature of bonding in actinoids

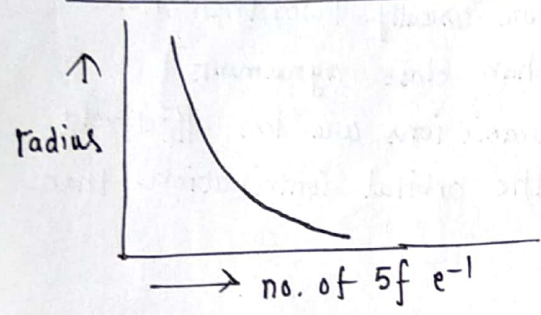
According to the modern view, $5f$ orbitals in actinides start filling from $_{91}\text{Pa}$ and not from $_{90}\text{Th}$ as it is evident from the valence shell electronic configuration of actinides. It is evident that, for the lighter members for eg. $_{89}\text{Ac}$ to $_{93}\text{Np}$, retain 6d electrons. The later tendency results both from the smaller energy separation between the $5f$ and 6d orbitals and from the difference in change in binding energy of the weakest bound 6d and $5f$ orbitals (electrons) with increasing atomic number.



From a qualitative picture of a variance in B.E. against atomic no., spectroscopic, chemical and other data tells that, $5f$ levels becomes progressively lower in energy compared to the 6d level with increasing atomic no. The $5f$ orbitals are deeply penetrating and are diffused at the periphery of the atom.

Hence the orbitals are somewhat perturbed at the presence of ligand field. It is well known that the energy difference between different levels decreases with increasing atomic no. Thus, in the actinides, the energies of the 5f, 6d, 7s, 7p orbitals are almost comparable. This suggests, that bonding in those compounds of actinides can involve any or all of the orbitals. This fact is evident that, the actinoids form complexes not only with anions such as X^- , SO_4^{2-} etc. but also with π -bonding ligands by the use of 5f-orbitals. (difference from lanthanoids: lanthanoids form no complexes or covalent compounds, in which 4f orbitals participate in bonding, instead, they form only ionic compounds).

Atomic and ionic radius

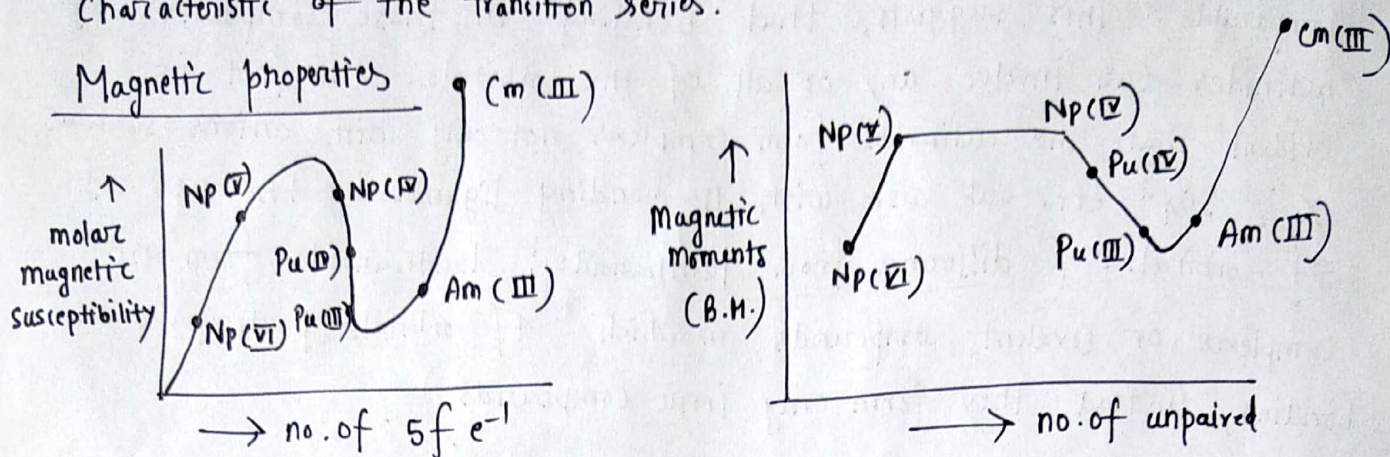


Crystal str. data provides the basis for ionic radii of the actinide elements. It may be noted that, for An^{3+} ions, there is actinide contraction analogous to lanthanide contraction. This is due to the successive addition of e^- in the inner f-subshell.

Colour of the actinide ions

Atomic no.	element	M^{3+}	M^{4+}	MO_2^+	MO_2^{2+}	MO_5^{3-}
89	Ac	Colourless				
90	Th		Colourless			
91	Pa		"	colourless		
92	U	Red	pink	colourless	Yellow	
93	Np	Blue-purple	Yellow-green	green	burgundy	dark green
94	Pu	blue-violet	orange-brown	Rose	Yellow to orange	dark green
95	Am	pink/yellow	Red/brown	Yellow	wine-coloured	
96	Cm	Pale green	—			
97	Bk	Green	Yellow			
98	Cf	Green				
99	Es					
100	Fm					

Open spaces indicates that, the corresponding oxdn. state are known to exist in soln. only. In addition to the simple hydrated cations, the actinides exhibit higher-valent oxy cation MO_2^+ , MO_2^{2+} and MO_5^{3+} . The wide variety of colours exhibited by actinide ions is characteristic of the transition series.



The magnetic properties of actinide ions are difficult to explain. The values of magnetic moments found experimentally are usually lower than those calculated using coupling scheme. [lanthanoids have close agreements]. This is because, the $5f$ electrons of the transuranic ions are less effectively screened from the crystal field which quenches the orbital contribution than $4f$ -electron of lanthanoids.

Complex formation

The degree of complex formn. order: $\text{An}^{4+} > \text{AnO}_2^{2+} > \text{An}^{3+} > \text{AnO}_2^+$

Complexing power of the ligands: $\text{F}^- > \text{NO}_3^- > \text{Cl}^-$
 $\text{CO}_3^{2-} > \text{C}_2\text{O}_4^{2-} > \text{SO}_4^{2-}$

Hydrolysis: The small, highly charged M^{4+} exhibit the greatest tendency to hydrolysis and complex formn. [eg. Pu^{4+} hydrolyses extensively].

The order of hydrolysis and complex formn. runs parallel for the ions. The MO_2^+ ion can almost be regarded as a large, singly charged cation of the alkali metal type. The actinide ion formn. Somewhat stronger complex ions than their lanthanide counterparts. Actinides form complexes with a large no. of organic substances and depends markedly on the oxidation states. A no. of important separation processes are based largely on the facts.

Spectra

(7)

The electronic spectra of the actinides arises from three types of electronic transitions: a) $f-f$ b) $f-d$ c) LMCT

The absorption spectra of lanthanides and actinides in aqueous soln. and in crystalline form exhibit very narrow $f-f$ bands in the near UV to near IR region of the electromagnetic spectrum. The transition in visible region gives rise to the observed colour of the ions. The $f-f$ absorption spectra of actinide ions provide distinct fingerprints of elements and oxdn. state and this has been extensively exploited for both qualitative and quantitative purposes. The allowed $f-d$ and CT transition for anions give rise to broad and fairly intense absorption bands. These are responsible for the deep colours of higher oxidation state complexes with polarisable ligands. Luminiscence has long been considered as a complementary technique to absorption spectroscopy. Self-luminiscence occurs due to excitation by the energy released from radioactive decay of Cm^{244} . Luminiscence has also been observed in the trichlorides of U, Np, Am, Cm when diluted with lanthanum fluoride.

Separation of actinides

1. Solvent extraction \rightarrow not in syll.
2. Precipitation technique \rightarrow not in syll.
3. Ion-exchange method:

Both cation and anion exchange have been utilised to a great extent for the recovery, separation and purification of all actinides, as in the case of complex forms. The uptake of various actinide ions vary in the order: $\text{MO}_2^+ < \text{M}^{2+} < \text{MO}_2^{2+} < \text{M}^{3+} < \text{M}^{4+}$

M^{4+} ions are absorbed strongly even from acid solutions by cation exchanger. The distribution ratio of trivalent cations of actinides do not differ widely and decrease with decreasing ionic radius. This is in contrary to the expectation and is due to increased hydration of the smaller cations. Inorganic exchanger like ZrPO_4 has been used for actinide separation. Unlike the organic resins, the exchanger does not discriminate An^{3+} from lanthanid (III) ions and the affinity increases with the radius of the naked ions rather than the hydrated one.